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OIL POLLUTION IN THE SEA: PROBLEMS FOR FUTURE WORK

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ABSTRACT

It is estimated that about one million tons of nonvolatile petroleum products are dumped into the ocean every year. Typically, these products congeal into slowly hardening lumps which are only gradually oxidized (over periods of months), and which can therefore drift for long distances. Technical problems associated with the enforcement of pollution control laws are discussed, and possible means are given for solving these problems, and for providing defenses against pollution. Data requirements for further studies are specified.

Enforcement of preventive legislation would be facilitated if it were possible to identify unequivocally the source of the pollutant. A scheme for doing this, involving the use of minute quantities (10^{-5} mole per ton of cargo) of tritiated hydrocarbon additives, is discussed. Potential health hazards, cost and instrumentation considerations, and other aspects of the use of such additives are surveyed. It is concluded that the technique poses no foreseeable health hazard, that it is economically feasible, and that the investment required for identification instrumentation is nominal.

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I. INTRODUCTION

This document contains a summary of what the members of the Jason Oil Pollution Study, during the summer of 1967, were able to find out about the sources and extent of oil pollution on the coast-lines and in the oceans. The information was obtained from many sources, including conversations with people knowledgeable in one area or another of the problem, written reports, newspaper articles, testimony before Congressional Committees, and so forth.

In the course of trying to track down data on oil pollution, it became clear that little systematic documentation of the problem exists. What measurements have been made of the amount or kind of oil pollution on the coast are confined to very localized regions. There are no data at all on the amounts of oil in the open sea. The sources of pollution are also not well understood quantitatively, and there is considerable dispute and uncertainty over whether or not some sources of oil in the sea contribute massively or not at all to the pollution problem. There is, therefore, a primary need to gather some good data, and this is the first recommendation we have to make. This recommendation, together with suggestions of other directions for future work, are elaborated in Section IV. Section II describes the sources that put oil into the sea, and includes some (very) rough estimates of quantities. Section III describes briefly what is known about what subsequently happens to the oil.

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II. SOURCES OF OIL IN THE SEA

A. NATURAL SOURCES

Some oil is emitted from natural seeps offshore. Several have
been found off the California Coast, and several more in the Gulf of
Mexico, associated with the offshore oil fields in these areas (Ref. 1).
Rates of flow from these are unknown.

B. SUNKEN SHIPS

Oil may also be released from sunken ships. The potential pollu-
tion is considerable. During World War II a total of 428 ships was
sunk off the East Coast of the United States, in the Caribbean and
in the Gulf of Mexico. The total tonnage was 2,270,000 tons, of which
nearly half was tankers (Ref. 2). The amount of oil in all these ships,
tanker and nontanker, is difficult to estimate, but it must come to
something of the order of a few million tons. It is estimated that
there are 61 sunken tankers containing nearly 10^6 tons of oil close by
the Atlantic Coast (Ref. 1). The potential pollution problem could be
severe; however, the rate of leakage is probably low enough to make
this source relatively unimportant overall.

C. DUMPING FROM TANKERS

In the process of discharging sea water ballast and of cleaning
oil tanks, tankers may dump oil into the sea. According to inter-
national convention, it is illegal to do this within 100 miles of the
U.S. coast, but there are essentially no enforcement procedures so it
is frequently done anyway. Also, as will be noted below, 100 miles is
not always far enough offshore to prevent the oil from reaching the
coastline.

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An outline of the procedure is the following (Ref. 3). A tanker arrives at a discharge port (usually a refinery) where its cargo is unloaded. Some oil, however, adheres to the tank surfaces and the sides of the piping, and this remains on board. The ship then leaves on its return voyage to a loading port. It is necessary for the ship to take on ballast to make it seaworthy, and sea water is used for this purpose. The water is usually stored in the empty oil tanks. The amount of ballast required depends on the weather, and varies from 1/4 of capacity to over 1/2 of capacity in very rough weather. Some of the oil remaining in the tanks used for ballast mixes with the ballast water. Two possibilities are now open. The tanker may proceed to the loading port, and dump the polluted ballast just before reaching it; or, if it is desired to arrive in the loading port with clean tanks (as is necessary if, for example, a different grade of oil is to be loaded), a cleaning procedure is gone through while the ship is en route. This consists of lowering a hot water spray machine into the empty tanks and washing out the oil residue. The residue is then either dumped, or transferred to a storage tank. Then new ballast is added to the clean tanks, the dirty ballast dumped from the dirty tanks, and the cleaning operation repeated for them. (In principle, the dirty ballast could also be transferred to a storage tank, by taking the time to allow the oil and water to separate and periodically dumping the clean water from the bottom of the tank. While this is a recommended procedure in many tanker companies (Ref. 3), it appears that in practice it is all too often considered to be too time consuming and too much trouble.) All tanks are now clean, and clean ballast is discharged upon arrival at the loading port. Here a new cargo is taken aboard, and the ship returns to a discharge port.

One can estimate the amount of oil coming from this source. The total world production of oil in 1966 was about 2×10^9 tons (Ref. 4). Of this amount, about half, or 10^9 tons, was transported by sea. Roughly 0.3 percent of the cargo remains in the tanks and piping when

a tanker is discharged (Ref. 1). If the tanks are cleaned, and the resulting sea-water oil mixture is dumped, one would expect about 3×10^6 tons of oil to be released into the sea per year. This number is probably an overestimate of the amount of pollution, however, for the following reasons:

1. Roughly 40 percent of the 10^9 tons carried is refined oil-- gasoline and such--and this tends to be oxidized very quickly in the sea.

2. Tanks are not cleaned on every voyage. It is estimated they are cleaned on only 20 percent of the trips (Ref. 1).

3. On the remaining 80 percent of trips, discharge of oil occurs only through the discharge of ballast water; this does not really clean out the tanks effectively, and removes only 15 percent of the oil residue in the tank (Ref. 1).

Altogether, it may be estimated that probably no more than 10^6 tons per year are dumped into the sea.
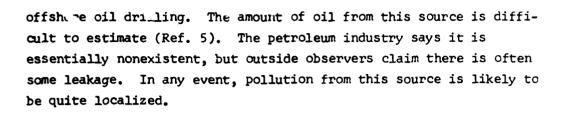
D. DUMPING FROM OTHER SHIPS

Nontankers also dump oil into the sea because of the practice of filling fuel tanks with sea water for ballast and then discharging this just before entering port, or in the harbor. Not much oil per ship is lost this way, but there are lots of ships. It is estimated that about 5×10^5 tons of oil/year come from this source (Ref. 1).

E. ACCIDENTS

Finally, oil appears from accidents. For example, the Torrey Canyon dumped 10^5 tons of oil into the sea. On the average, total pollution from this source is likely to be small compared to the sources mentioned above; nevertheless, accidents can cause severe local problems.

F. DRILLING OPERATIONS

There is, in principle, also the possibility of pollution from

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offshore oil drilling. The amount of oil from this source is diffi-
cult to estimate (Ref. 5). The petroleum industry says it is
essentially nonexistent, but outside observers claim there is often
some leakage. In any event, pollution from this source is likely to
be quite localized.

III. WHAT HAPPENS TO OIL IN THE SEA?

Immediately after discharge, the oil forms into large patches surrounded by a thin film composed of the more volatile ingredients in the oil. This thin film is oxidized by bacteria very quickly, usually within a few hours. The remaining oil gradually congeals into lumps which slowly harden. The lumps are also oxidized by bacteria, but the rate for doing this is quite slow because of the small surface-to-volume ratio of the lumps. These lumps are frequently eventually deposited on the shoreline. Liquid oil comes ashore only rarely--only when it is released quite close to shore (Ref. 6).

To get an idea of numbers, the following is the result of one year of observation on the Florida coastline, of three 100-foot stretches of beach (Ref. 6).

1. The total amount of oil observed in all forms was about one ton per mile per year, and new oil came ashore in one form or other on 95 percent of the days.
2. Liquid oil was found on only one day.
3. Soft sticky lumps made up nearly 30 percent of the total (the remainder was in hard lumps), and this type of oil came ashore on 60 percent of the days.
4. Most of the lumps are small, of the order of a centimeter across, but lumps up to 5 feet in diameter have been observed.

The time for bacterial destruction of oil lumps several centimeters in diameter is, as stated before, generally very long. The bacteria density in the open sea is of the order of several organisms/cc. The reproduction time varies from 15 minutes to several hours, depending on, among other things, the temperature. The rate of

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oxidation by bacteria is also very temperature-dependent, but a rough guess is stated to be 5×10^{-12} mg of oil/organism/hour at $25^{\circ}C$. This rate can only be achieved if the oil is broken into small lumps of the order 2 to 3 microns in size; however, after a short time (a few hours) in the sea, actual oil particles are of the order of several millimeters across (Ref. 7).

Thus lumps of oil have a long life (of the order of months) in sea water (Ref. 6), and hence can drift long distances with the currents. The direction and speed of currents vary with the season of the year as well as with the geographic locality, but in many places it is quite reasonable to expect currents of several miles per day, directed onshore from several hundred miles offshore. Spillages of oil this far out at sea may then still be a source of pollution of the coastline.

IV. SUGGESTIONS AND RECOMMENDATIONS

A. TANKER-CAUSED POLLUTION

This is likely to be the most important source of pollution, so we will start here.

1. Legal Aspects

The present legal situation is that tankers are prohibited from flushing tanks or dumping polluted ballast water in various regions, including the North Sea and a strip roughly 100 miles wide off the U.S. coast. Beyond this, any dumping is legal, and even with these prohibited regions dumping of "nonpersistent" petroleum products, such as gasoline, is allowed.

However, pollution of the shore from any dumping of oil, even if purely accidental, is (or shortly will be) the legal responsibility of the ship operator, and the operator is required to pay all cleanup costs. (In framing this law, it is evidently implicitly assumed that no coastal pollution can occur from dumping more than 100 miles off-shore, and this is a false assumption.)

Within this legal framework, the enforcement problem is clearly very difficult. Detection of oil dumping at the time it occurs is almost impossible, and without positive identification of the source of any pollution which occurs, no responsibility can be fixed.

2. Removing Pollution

The only defense remaining is to clean up the oil after it appears in the sea and, hopefully, before it arrives on the shore. This requires:

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a. Detecting the oil as soon as possible. A survey mechanism is needed which can cover large areas of ocean. Since oil slicks in the sea rapidly disappear, with the oil forming into small lumps, visual scanning probably will not work. But other detection schemes, perhaps satellite-based, can probably be invented. Work is needed here.

b. Identifying in which areas of the ocean oil pollution can be a threat to the coast. This requires a knowledge of winds and ocean currents, and continued monitoring.

c. Destruction of those patches of oil which could be dangerous. Here the most efficient method may well be to use oil-eating bacteria. These could perhaps be dispersed from airplanes using BW techniques. However, making the oil into small enough blobs to permit effective attack by the bacteria may be difficult. Perhaps some chemical additive to change the surface tension at the oil-water interface can be used together with the bacteria, although the amount of any chemical agent required is probably prohibitive. Alternatively, tankers could be equipped with some sort of device for "atomizing" the oil before it is discharged, although one would, in the present legal environment, have to depend on the good will of the ship operators to install and use it. Work on the design of such devices would be of value. The most obvious place to begin is in the design of nozzles for the hoses used in dumping the oil overboard; one wants to arrange that the oil is ejected as an oil water emulsion.

The kind of bacteria to be used should be the subject of intensive research. Bacteria occurring naturally in the sea do eat oil, but it should be possible to grow new varieties of bacteria which are optimized for the purpose. Some work in the direction of developing bacteria specifically suited to oil already exists; for example, yeast for use as chicken

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feed is grown commercially in crude oil in both France and China.

If sufficiently efficient bacteria can be developed, it might be possible to introduce them into the tanks of a tanker on its in-ballast voyage, and use the bacteria to destroy the oil in the empty tanks and/or in the ballast-filled tanks. Then the harmless residue could be dumped, or conceivably, in the French or Chinese pattern, it might have some commercial value. Such an application would require fast acting bacteria, since the time available for oxidation of the oil would be at most a couple of weeks.

d. Containment. It may be possible to contain patches of oil, perhaps by various floating physical barriers, long enough to allow effective bacterial action. Such containing devices exist now for use in harbors, but none which can cope with waves in the open sea. There may be an opportunity for some work here.

3. Enforcement of Regulations

If the legal framework could be changed to prohibit the dumping of oil anywhere in the sea, the enforcement problem becomes much easier.

The simplest way of ensuring that no oil has been dumped is simply to require that each tanker arriving in port in ballast be inspected, and that it have on board, in some tank, roughly the amount of oil sea-water emulsion to be expected from tank cleaning based on the load carried on the previous voyage, and that all other tanks, including those used for ballast, be clean. Since tankers are already inspected upon arriving in port anyway, for other reasons, this should be easy to implement.

To enforce the responsibility for cleanup costs in the event of any pollution occurring on the coastline, it may be possible to use chemical tracers. A particular combination of chemicals would be assigned as a signature to each tanker, and mixed in with each cargo

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at the time of loading. Any oil found on beaches would then be analyzed, and the ship of origin identified.

Such tracer chemicals would have to have the following properties:

a. They must be soluble in oil.
b. They must be identifiable in concentrations like 10^{-7}, so that only a few pounds are required for each tanker load, yet they must not occur naturally in any kind of oil, except in much lower concentrations.
c. They must not be soluble in sea water.
d. There must be enough combinations available to mark each of the roughly 4000 tankers now in use. This requires at least 12 different tracer chemicals.

One suggestion for such a tracer scheme is described in Appendix A.

4. Insurance

An alternative method which has been proposed is to not bother to identify the source of any pollution which occurs, and to pay for the cleaning costs through an insurance scheme to which all ships are required to contribute, thus spreading the costs over the whole oil transportation industry (Ref. 8). The contributions would be calculated as a function of how much oil a particular ship carried, and its route. This would encourage a self-policing attitude by the ship operators, in order to reduce the insurance costs.

5. Shore Facilities

A necessary adjunct to any system requiring tankers to bring the residue of cleaning operations or dirty ballast into port will be facilities for disposal on shore. In some cases, if a refinery is present, the residue can be processed and the oil recovered. Otherwise there must be some sort of dump available. At present, only a limited number of crude oil loading ports have such facilities, and

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the volumes which can be handled are small. The ship would therefore
be required to retain the waste material on board until it arrived
at a refinery or a port with disposal facilities where it could be
discharged. This would probably mean some increase in operating
expense.

B. POLLUTION FROM OTHER SOURCES

Possible defenses against the other sources of oil pollution
have mostly already been mentioned in connection with tankers.

For pollution from natural seepage, continuous deposition of
bacteria might help.

For pollution from accidents, the discussion under Sections
A-2c and A-2d is applicable.

The pollution from sunken tankers is probably not very important,
but it is perhaps possible to locate the tankers and pump out the oil.
This may even be economically rewarding, and it would at least be a
test of the Navy's developing underwater technology. The sunken
tankers of interest are all on the continental shelf, and hence not
in deep water. The location problem should therefore be relatively
easy, particularly since the rough location already exists in Navy
records from World War II.

In Section II it was noted that the amount of pollution from
ballasting fuel tanks with sea water in ordinary ships is almost
comparable to that from tankers. The long-term cure here is probably
to design ships with separate fuel and ballast tanks.

For the short term, it may be useful to attempt to separate the
oil remaining in the fuel tanks from the sea water ballast prior to
discharge of the ballast. If this could be done, the water could be
discharged (up to a point where some given acceptable amount of oil
is present) and the oil retained in the fuel tanks, to be mixed with
the new oil which is to be loaded for fuel. Unfortunately, the most

obvious method of separation, namely gravity, is difficult because fuel oils now in use have a specific gravity of 0.998 (Ref. 1). But perhaps some other separation technique could be invented.

Aside from this, it is unlikely that much can be done about ordinary ships. Prohibiting the discharge of oily ballast water at sea or in harbors is possible only if facilities exist to dispose of it on shore, or under controlled conditions. But the number of nontankers operating all around the world and the number of ports in use are so large that such facilities in useful numbers would be quite expensive to construct.

C. DATA REQUIREMENTS

Finally, as remarked in the Introduction, a world-wide study to provide some reliable numbers on both the source and amount of oil pollution would be highly desirable. What is needed is, among other things:

1. An estimate of how much oil/year comes ashore on the entire coast, and an attempt to find the areas of heaviest concentration.

2. An estimate of how long the oil has survived in the sea before coming ashore, and an assessment of how much oil exists in the open sea.

3. A survey of natural seeps, both as to location and flow rates.

4. A survey of offshore drilling to see whether there really is pollution from this source.

5. A survey of tanker operations to see how many tankers do in fact dump polluted ballast into the sea.

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ACKNOWLEDGMENT

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APPENDIX A

A METHOD FOR LABELLING TANKER CARGOS

Robert Gomer

I. INTRODUCTION

The pollution of shores by oil from various sources is a problem
of constantly increasing magnitude. As was noted in the preceding
discussions, a major portion of this pollution is believed to result
from tanker and other ship discharges, accidental or otherwise.
The effectiveness of preventive legislation could be greatly enhanced
by a method to label oil cargos. A resolution corresponding to single
shiploads, or even a resolution corresponding to weekly or monthly
refinery or oil-field outputs would permit tracing the sources of
pollution. Labelling methods would also be of great usefulness for
diagnostic and enforcement purposes for many other pollution problems.
In this note the specific problem of labelling nonvolatile tanker
cargos (crude oil, bunker C, etc.) is discussed.

II. REQUIREMENTS

To be practical, a labelling method must meet the following
requirements:

1. It must not pose a health hazard.
2. The amounts of label added must be reasonably small and
    reasonably cheap.
3. Labelling and "reading" of the labels must be quick and
    relatively simple.
4. Labelling additives must not cause subsequent complications,
    such as poisoning catalysts in refinery processes. (This
    rules out neutron activation analysis of metal additives
    for instance.)
5. Labelling must not be interfered with by substances already
    present in the cargo.

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6. A sufficient number of labels must be available to handle the required volume.

7. Labelling must be nearly tamperproof and must be unequivocal.

III. PRINCIPLE OF THE PROPOSED METHOD

Despite these rather formidable requirements there is a relatively simple and inexpensive method which meets them, namely tritium labelling, which seems first to have been advocated as a general tracing method by Willard Libby; I am indebted to my colleague Anthony Turkevich for pointing it out to me.

Basically, the method consists of adding tritium labelled compounds to the cargo, isolating these from a sample of (for instance) oil slick and determining the H^3H^1 ratio. To illustrate the amounts required, let us assume for the moment that a single tritiated compound will be added, that a 1-gram sample of oil slick will be collected and that an activity of 100 counts/minute in this sample is required for analytical purposes. (If necessary a considerably lower activity could be used, but 100 cpm is a comfortable level.) The half life of H^3 is 12 years of 6×10^6 minutes, so that the number of H^3 atoms in the sample must be 6×10^8 for a decay rate of 100/minute. If a cargo of 100,000 tons (10^{11} grams) is to be labelled, 6×10^{19} H^3 atoms, or 10^{-4} moles (i.e., 3×10^{-4} g) would be required. Let us assume that the labelling compound is a hydrocarbon, tritiated to an extent of 10^{-4} so that 1 mole of dilutely tritiated compound is required. This would amount to 200 to 500 g of compound for 100,000 tons of cargo!

In order to provide a sufficiently large number of labels, the actual procedure could be somewhat as follows. An "alphabet" of "letter" compounds, A , B, C, . . . N is selected. A label consists of a zero to n letter word (four letter words being chosen with cir-cumspection, of course) of tritiated letter compounds, say A_TC_T, or $B_TF_TG_TN_T$, etc. The sample to be analyzed is mixed with a quantity of wholly untritiated alphabet soup, containing all the letters, and subjected to a separation procedure. All the letter compounds are then

examined for tritium activity (the tritiated letters in the sample
being carried along in the separation with the untritiated compounds
added as carriers) and the labelling word thus obtained. The number
of "words" obtainable from an alphabet of $\underline{n}$ letters is

$$v = \sum_{a=0}^{a=n} \frac{n!}{a!(n-a)!} \qquad (1)$$

since any given group of $\underline{a}$ letters regardless of order (which cannot
be determined) gives a single "word." The leading term in this
expression corresponds to $\underline{a} = n/2$ and is approximated by

$$\log v_{n/2} \doteq n \log 2 + (1/2) \log (\pi n/2) \qquad (2)$$

For $n = 10$, $v_{n/2} = 253$ (the total number of words being 1025);
for $n = 15$, $v_{n/2} = 6000$; and for $n = 20$, $v_{n/2} = 1.8 \times 10^5$.
Thus if 10 to 20 suitable letter compounds can be found, the number
of words, or signatures that can be made up seems adequate for any
foreseeable demand.

IV. A SPECIFIC SCHEME

While many methods of implementing this general scheme are
possible it may be illuminating to sketch ⌐ specific procedure appli-
cable to tanker cargos. The choice of labelling compounds is governed
by the requirements (in addition to others set forth in Section II)
that they must not be water soluble, must be oil soluble, and must
have sufficiently low vapor pressures not to evaporate from oil slicks.
Further, they must be tritiable, must not exchange H^3, and must be
separable. The simplest (but by no means only) class of compounds
meeting these requirements are straight-chain hydrocarbons from say
C_{15} to C_{30}, which are chosen here more for illustration than
necessarily for optimum ease of implementation. The procedure consists
of preparing triatiated hydrocarbons, adding these to the cargos in
the desired combinations (words) in quantities of about 10^{-5} mole/ton
of cargo. When a sample to be analyzed is collected, a known amount

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of equimolar alphabet mix (i.e., C_{15} through C_{30} hydrocarbons) is added, the augmented sample subjected either to fractional vacuum-distillation in a suitable micro-column, or passed through a "prep-scale" (i.e., suitable for handling samples of the order of 1 g or so, in contrast to the more usual sample size of 10^{-6} g) gas-chromato-graph, calibrated for this hydrocarbon range. The emerging hydro-carbons are burned to CO_2 and H_2O, the latter converted to H_2 (say by passing over hot uranium) and counted.

If the total amount of $C_nH_{2(n+1)}$ (tritiated to a mole fraction of 10^{-4}) in the collected sample is x moles, and if b moles of un-tritiated $C_nH_{2(n+1)}$ were added as carrier, the H^3/H^1 ratio in the counted hydrogen is

$$H^3/H^1 = \frac{x10^{-4}}{(b+x)2(n+1)} \qquad (3)$$

If b >>x (which would normally be the case),

$$H^3H^1 \cong \frac{10^{-4}}{2(n+1)} \quad (x/b) \qquad (4)$$

so that an absolute H^3/H^1 ratio in the unaugmented sample cannot be determined unless x is known. While this would be difficult to do absolutely, x can be approximately determined by pilot experiments on the concentration, viz., dilution of labels in oils subjected to sun and sea. In any case it suffices to determine the H^3/H^1 ratios for various alphabet compounds, which are proportional to $1/(n+1)$ as shown by Eqs. 3 or 4. If the variation in x for different letters due to evaporation, reaction, etc., is only slight, the relative H^3/H^1 ratios of the different "letters" can also be used, either to set limits of reliability, and/or--by varying the quantitative com-position of the signature--to add another dimension to the labelling.

If desired, concentration of the letter compounds in the collected oil sample can be effected prior to analysis. Just as an example, one might use as letters alcohols and/or fatty acids in ester form (soluble

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in the cargo.) After adding untritiated esters as carriers and saponifying, the free alcohols and/or acids could then be separated from the rest of the oil sample by solvent extraction, followed by separation of the letter compounds, from each other (if necessary after catalytic reduction to hydrocarbons.) In this way a much larger sample than 1 g could easily be processed, thus decreasing the total amount of H^3 required by at least an order of magnitude.

Undoubtedly, many other refinements could be devised. The point of this section is to show that a feasible scheme could be implemented right now with off-the-shelf equipment and known techniques.

V. COMPATIBILITY OF METHOD WITH GENERAL BOUNDARY CONDITIONS

We now examine tritium labelling from the viewpoint of the various criteria laid down in Section II.

A. HEALTH HAZARDS

Tritium decays by emission of an 11 kV beta particle, so that its activity poses no external hazard to tanker crews or to other personnel even if in direct contact with labelled cargo. It is necessary to examine in more detail the potential health hazard posed by the ultimate appearance of H^3 in the geosphere as water as the result of the eventual combustion of most of the labels. If five-letter words are taken on the average, and if an activity of 100 cpm per letter in a 1-g sample is required, the amount of H^3 per ton is $5 \times 6.10^{14} = 3 \times 10^{15} H^3$ atoms/ton of cargo or 2.2×10^{-4} curies/ton. The annual shipped oil flow of the world is $\sim 7.10^8$ tons/year. If this entire amount were to be labelled, $2.10^{24} H^3$ atoms/year would be required. This corresponds to an activity of 1.5×10^5 curies/year. The maximum amount of H^3 activity in the geosphere would be that resulting at steady state, i.e.,

$$H^3_{max} = Y\tau \qquad (5)$$

where Y is the rate of H^3 release, and τ its half life with respect to beta decay (12 years). Thus $H^3_{max} = 1.5 \times 10^5 \times 12 = 1.8 \times 10^6$ curies or 2.4×10^{25} H^3 atoms. The resulting body concentration of H^3 activity can be estimated as follows. If we assume an average of 75 kg of H_2O per human body, we need only the amount of water with which we are in equilibrium to find the H^3 content, since there will be no appreciable fractionation of heavy water. The total amount of water in the atmosphere is estimated to be 0.13 geograms (0.13×10^{20} g) and the annual amount discharged into the oceans is estimated to be 0.18 geogram. Consequently, we can take as a safe minimum amount of water into which H^3 would be discharged, and with which we are in contact, the water content of the atmosphere. On this basis, the H^3 activity per human body would be at most 1.8×10^6 $(7.5 \times 10^4 / 1.3 \times 10^{19}) = 10^{-8}$ curies. In actual fact, the weight of water to be considered is more likely to be 1 to 10 percent of the total in the geosphere, or 140 to 1400 geograms. If these figures are used, the eventual body level from cargo labelling would be 10^{-11} to 10^{-12} curies, which is to be compared with the present level of 4×10^{-10} curies (based on the present worldwide H^3/H ratio of 10^{-18}). Thus tritium labelling would increase present levels by 2 percent at most. The permissible permanent H^3 level in adults is estimated as 5 millicuries, which is 10^8 times the level which could result from labelling.

It is also necessary to consider the problem of local concentrations, for instance in areas subject to inversion layers. Let us assume as a representative example a city of 2000 km^2 area in which 1 million cars consume 28 kg of gasoline (10 gallons) each per day. Let us assume the height of the inversion layer to be 100 m (300 feet) which is, of course, extremely conservative. 2.8×10^4 tons of petroleum products if fully labelled would contain $2.8 \times 10^4 \times 2.2 \times 10^{-4} = 6$ curies of H^3 activity. If each of the city's hypothetical 6 million inhabitants got his fair share of this he would ingest 1 microcurie/day. In fact the amount is much less of course. Let us assume that all the H^3 appears in the city's air, i.e., in a volume of $2000 \times 10^6 \times 10^{22} = 2 \times 10^{11}$ m^3 and that city air has a half lift with respect to

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replacement by fresh air of 1 day so that the average H^3 level is roughly equal to its daily production. At a breathing rate of 6 liter/minute, an adult inhales 9000 liters of air per day so that the amount of tritium activity inhaled per day is $6(9000/2 \times 10^{14}) = 3 \times 10^{-10}$ curies/day. If it is assumed that all the inhaled H_2^3O is retained, the eventual body level of H^3 will be determined by the turnover of body water; the projected worldwide H^3 concentration is sufficiently small to permit the assumption that ingested drinking water is effectively free from H^3 for the purposes of this calculation. The half-life of water in the body is about 10 days, so that the steady-state concentration of H^3 in the area under consideration would not exceed 3×10^{-9} curies, or ten times the present level. This is negligible as already pointed out.

The assumptions made in this section have been extremely conservative, in order to err on the safe side. Thus, only a small faction of the total oil cargo flow would in fact need to be labelled, and if even uncomfortable H^3 levels should result discontinuation of labelling would soon reduce these, because of the short half-life of H^3. Further, the requirement of 1-g samples could easily be changed to 100-g samples by preconcentration and other techniques, thus reducing the total H^3 requirements by two orders of magnitude. Local concentrations were calculated on the assumption of fully labelled petroleum products and high petroleum consumption rates. In summary, H^3 labelling poses no foreseeable health hazard, and could easily be monitored and discontinued if it should threaten to do so.

B. AMOUNTS OF H^3 REQUIRED, COST AND AVAILABILITY OF LABELS

The total amount of H^3 required per year in the form of labelling compounds has already been estimated as 2×10^{24} atoms, i.e., 1.5×10^5 curies or ~ 10 g of H^3. Even if 10 times this amount were actually needed to prepare this labelled compounds, the world requirement would stand at 100 g/year. Pure H^3 is currently available commercially at a price of \$15/curie (after the first, which is \$50/curie). Thus, the cost of H^3 per year for the entire oil shipping of the world would be

at most $\$1.5 \times 10^6 \times 15 \simeq \$20{,}000{,}000$ or $2.2 \times 10^{-3} \times 15 \simeq 3$ cents/ton. This calculation has assumed that a tenfold excess of H^3 is needed over that to be incorporated. There are chemical methods (for instance, saturation of double bonds) in which there is essentially no tritium dilution so that unused tritium can be recovered undiluted. This would reduce the cost by at least a factor of five from the upper limit quoted above.

Hydrocarbons of 99 percent purity in the C_{15} and above range are presently available at prices of the order of $\$30$/kg. Assuming a total requirement of 20,000 kg for the annual world oil flow, the cost would be $\$600{,}000$ or ~ 0.1 cent/ton of cargo. If the price of the hydrocarbons were doubled to include the cost of the tritiating manipulations (exclusive of H^3 cost) the total cost per ton of cargo would be 0.8 to 3 cents, depending on the actual amount of H^3 required. It should further be pointed out that the H^3 price quoted above is somewhat artificial since H^3 could certainly be made available at a greatly reduced cost if cargo labelling were felt to be in the national interest.

C. EASE OF LABELLING AND READING

The amounts of label compound to be added to typical cargos are extremely small so that proper mixing would have to be insured by diluting the signature in stages, i.e., dissolving the signature mix first in, say, 10 gallons of solvent, diluting this up to 100, or 1000 gallons, and then drip-injecting this or a further diluted mixture into the loading stream. Such procedures are wholly within existing technology.

The analysis of collected samples has already been discussed and shown to be very straightforward. There are no special problems connected with collection of 1 to 1000-g samples of oil slicks or other residues.

The instrumentation required for one analytical station would consist, in addition to routine laboratory equipment, of a separator,

say a gas chromatograph ($5 to $50,000) and counting equipment ($5 to $10,000) or to an equipment cost of not over $60,000 per station, and possibly much less. Assuming that separation and counting take of the order of a day, a central laboratory capitalized at $1,000,000 could handle at least ten samples per day, and possibly many more by proper scheduling of the various stages of analysis. The process could be nearly automated, or in any case would not require more than five technicians. Thus, for a capital investment of $1,000,000 and an annual budget of roughly $100,000 it should be possible to process over 3000 samples per year.

D. INTERFERENCE WITH SUBSEQUENT USES OF CARGOS

Labels in the form of hydrocarbons or other organic compounds containing no heavy metals present only an infinitesimal perturbation of the original composition. In fact most of the contemplated additives would already be present in untritiated form in crude oil or other heavy oils. Thus, no chemical contamination need be feared.

One must also consider the possibility that the presence of weak betas might catalyze various reactions. The number of moles of H^3 per ton of cargo has been shown to be $\sim 10^{-9}$. Assuming an energy requirement of 30 eV per ion pair, an 11 kV beta would create $11,000/30 = 400$ ion pairs. Thus the total number of ion pairs per ton would be 4.10^{-7} mole. Assuming the very high chain length of 10^3 per initiated reaction (it would be closer to unity for most cargos, or subsequent products) there would be a total of 4×10^{-4} moles of reactants per ton of cargo. Assigning the reactant an average molecular weight of 500, a total of 0.2 g per ton of cargo, or 2×10^{-7} g per gram, would react.

Alternately, the so-called g-number (number of molecules reacted per 100 eV of energy deposited) for hydrocarbons and similar substances is of the order of 3, so that 330 reactions per H^3 can be postulated. This reasoning leads to $330 \times 10^{-9} = 3.3 \times 10^{-7}$ moles of reactant/ton cargo, which differs from the previous estimate essentially by the

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omission of a chain length. In either case, the amounts reacted, either in the crude oil, or in subsequent products, are totally negligible.

E. INTERFERENCE WITH THE TECHNIQUE BY CARGO COMPONENTS

Since the half-life of tritium is twelve years, crude oil, being considerably older than that, is wholly free of H^3. Heavy refinery products are in general the residues of distillation, rather than the result of chemical treatment with hydrogen exchangers and thus may also be expected to be substantially free from H^3. Somewhat more serious would be the problem of H^3 introduced into refinery products by prior labelling of crude oil. This would be of concern only for heavy residues and might necessitate labelling the latter with a different class of alphabet compounds from that used for crudes. It is beyond the scope of this note to consider this in detail, but it should not be very difficult to devise several different alphabets for such purposes.

F. ADEQUACY OF LABEL NUMBERS

It has already been pointed out that a 20-letter alphabet provides of the order of 10^6 different labels. If the average tanker voyage is 1 month, and if the total number of tankers to be labelled is 4000, something like 50,000 labels per year would be a maximum requirement. Considering that the same labels could probably be used simultaneously in different parts of the world, and that not all tanker runs would require labelling, this number is probably much too high. Since the world consumption of refinery products is at least comparable to the annual oil flow, it seems reasonable to assume that the same labels could be used over again after a year or so. In view of these facts, there seems no problem in making an adequate number of labels from the available supply of letter-compounds.

G. RELIABILITY

It would be difficult to falsify labels because mixing could be accomplished only at refineries or loading facilities, which could be subjected to inspection. Many major oil producers profess interest in preventing pollution and thus would be unlikely to attempt subversion of the control system. Since there is no exchange of H^3 in hydrocarbons, or in other properly chosen letter-compounds, even at the temperatures used in steam cleaning tanker holds, there is little possibility of mutation of signatures. A further advantage of H^3 labelling is the fact that the weakness of the emitted beta would make it virtually impossible for captains to determine whether their cargo had been labelled or not, since a simple counter such as might conceivably be available to captains would not detect 11 kV betas.

VI. POLITICAL, ADMINISTRATIVE, AND ECONOMIC ASPECTS

This note concerns itself primarily with the technical feasibility of cargo labelling, and with its cost in a narrow sense. The questions of where and how to install labelling and collection stations, what resolution to aim for, whether to attempt this on a national or international basis, and the total cost of a system, are outside the intended scope. An equally important question not considered here concerns the merits of labelling relative to other enforcement aids, such as careful bookkeeping on cargos. In defense of this restricted scope, the mere fact that labelling is technically feasible and the implied threat to potential violators could be of importance in the prevention of pollution.

VII. CONCLUSION

Tritium labelling of cargos provides an effective and cheap method of tracing pollutants. The method is free from health hazards and other objections, and could be readily adapted to a number of other uses.

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13. ABSTRACT

    It is estimated that about one million tons of nonvolatile petroleun products are dumped into the ocean every year. Typically, these products congeal into slowly hardening lumps which are only gradually oxidized (over periods of months), and which can therefore drift for long distances. Technical problems associated with the enforcement of pollution control laws are discussed, and possible means are given for solving these problems, and for providing defenses against pollution. Data requirements for further studies are specified.

    Enforcement of preventive legislation would be facilitated if it were possible to identify unequivocally the source of the pollutant. A scheme for doing this, involving the use of minute quantities (10^{-5} mole per ton of cargo) of tritiated hydrocarbon additives, is discussed. Potential health hazards, cost and instrumentation considerations, and other aspects of the use of such additives are surveyed. It is concluded that the technique poses no foreseeable health hazard, that it is economically feasible, and that the investment required for identification instrumentation is nominal.

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